DIVISION OF ENGINEERING AND GEOSCIENCES

Materials research in the Division of Engineering and Geosciences is sponsored by two different research programs, as described below.

The BES Engineering Research Program was started in 1979 to help resolve the numerous serious engineering issues arising from efforts to meet U.S. energy needs. The program supports fundamental research on broad, generic topics in energy related engineering-topics not as narrowly scoped as those addressed by the shorter term engineering research projects sponsored by the various DOE technology programs. Special emphasis is placed on projects which, if successfully concluded, will benefit more than one energy technology.

The broad goals of the BES Engineering Research Program are: (1) To extend the body of knowledge underlying current engineering practice so as to create new options for enhancing energy savings and production, for prolonging useful equipment life, and for reducing costs without degradation of industrial production and performance quality; and (2) To broaden the technical and conceptual base for solving future engineering problems in the energy technologies. The DOE contact for this program is Oscar P. Manley, (301) 903-5822.

The BES Geosciences Research Program supports research that is fundamental in nature and of long-term relevance to one or more energy technologies, national security, energy conservation, or the safety objectives of the Department of Energy. It is also concerned with the extraction and utilization of such resources in an environmentally acceptable way. The purpose of this program is to develop geoscience or geosciences-related information relevant to one or more of these Department of Energy objectives or to develop the broad, basic understanding of geologic materials and processes necessary for the attainment of long-term Department of Energy goals. In general, individual research efforts supported by this program may involve elements of several different energy objectives. The DOE Contact for this Program is William C. Luth, (301) 903-5822.

ENGINEERING SCIENCES RESEARCH

MATERIALS PROPERTIES, BEHAVIOR, CHARACTERIZATION OR TESTING

141. **BOUNDS ON DYNAMIC PLASTIC DEFORMATION**
$194,411
DOE Contact: Oscar P. Manley, (301) 903-5822
Argonne National Laboratory Contact:
C. K. Youngdahl, (312) 972-6149

Analytical studies are being performed to develop load correlation parameters which can be used in approximating or bounding the dynamic plastic deformation of structures. In many applications where the load is transmitted to the structure through a fluid, details of the load history and spatial distribution significantly affect the final plastic deformation. The objective of the program is to devise load correlation parameters based on various weighted integrals of the time-space load distributions which can be used to characterize the effects of the load without resorting to detailed numerical analysis. These load correlation parameters have three important uses: to perform design and safety analyses of structures over a wide range of design variables and loadings; to validate computer programs which have a nonlinear dynamic plasticity capability; and to correlate experimental simulations with actual or predicted events. The dynamic plastic deformation of some basic structural configurations will be analyzed for loadings which vary both in magnitude and region of application with time. Load correlation parameters will be hypothesized and their usefulness in predicting final plastic deformation will be determined. The analyses will be based initially on a rigid, perfectly plastic material model and small deformation response, but will be extended to include strain hardening, and initial elastic response period, and large deformation interactions.

Keywords: Plastic Deformation

142. **CONTINUOUS DAMAGE MECHANICS - CRITICAL STATES**
$50,945
DOE Contact: Oscar P. Manley, (301) 903-5822
Arizona State University Contact: D. Krajcinovic,
(602) 965-8656

The research during the fourth, and last, year of the research was focused almost entirely on the two tasks: (1) response of microcrack weakened solids in the vicinity of the critical state, and (2) initial exploration of the use of Preisach model in fatigue analyses.

The studies of critical states were concentrated on fundamental issues such as the determination of the proximity parameter, universal parameters, order parameter and differences between the elastic and traditional (conduction) percolation problems. It was demonstrated that the second order phase (connectivity) transition takes place only in stress (load) controlled conditions. In contrast, localization (emergence of shear bands) of the deformation occurs in the strain (displacement) controlled tests.

Initial exploration of the Preisach model were focused on ductile behavior using parallel bar models. Important conclusions were related to the thermodynamics of the process, including differences between locked-in and dissipated work.

Keywords: Metals: Ferrous, Fracture, Fatigue, Creep

143. **AN INVESTIGATION OF THE EFFECTS OF HISTORY DEPENDENT DAMAGE IN TIME DEPENDENT FRACTURE MECHANICS**
$23,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Battelle Memorial Institute Contact: F. Brust,
(614) 424-5034

The demands for structural systems to perform reliably under severe operating conditions continue to increase. Modern energy production facilities experience degradation and damage because they operate in severe high-temperature environment where time dependent straining and damage may lead to structural failures. The goal of this research is to study the high temperature damage and failure processes and to further develop a method for predicting this behavior in an effort to increase structural life. In particular, we focus on time dependent damage which occurs under history-dependent loading conditions, i.e., transient conditions.

The types of time dependent (creep) damage considered in this program include: sustained load creep, variable load creep, and variable load creep with thermal gradients. During the first year of this study, the implications of using Norton's creep law on various integral parameters used to characterize crack tip phenomena were evaluated as a function of time. Other constitutive laws for time dependent materials such as those of Murakami and Ohno are being implemented into the finite element code. In addition, constitutive property data and high temperature creep crack growth data are being obtained on stainless steel. These experiments will be used to verify analytical long-term Department of Energy goals. In general, individual research efforts supported by this program may involve elements of several different energy objectives. The DOE Contact for this Program is William C. Luth, (301) 903-5822.

ENGINEERING SCIENCES RESEARCH

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The results from this work will be used by practicing engineers to enhance the life of high temperature structural systems during the design phase.

Keywords: Fracture Mechanics, History Dependent Damage, High Temperature

144. **MICROMECHANICAL VISCOPLASTIC STRESS-STRAIN MODEL WITH GRAIN BOUNDARY SLIDING**
$0
DOE Contact: Oscar P. Manley, (301) 903-5822
University of Connecticut Contact: E. H. Jordan, (203) 486-2371

The first part of this project has focused on developing and experimentally verifying methods of predicting the deformation response of polycrystalline metals from models of single crystal deformation, based on crystallographic slip. In the ongoing research, the goal is to try to predict the degree of heterogeneity of deformation and verify these predictions experimentally. The existing self-consistent model is to be completed by a second model based on periodicity which is expected to be both more realistic and more computationally burdensome. The degree of heterogeneity of deformation will be studied by different experimental techniques. Neutron diffraction experiments are planned in which diffraction from a few grains at a time is studied to determine lattice strains in individual grains. Many grains will be surveyed to get a statistical measure of heterogeneity of grains including no surface grains. The Moire strain analysis will alsc be done on large grained samples. The material studied is the same one used in the first phase, so that all the single crystal mechanical properties are accurately known. The data collected will provide a unique complete set of data to test the ability of the models in this program and other models with respect to their ability to predict the degree of heterogeneity of deformation. Comparison of the Moire data and the neutron diffraction data will also provide insight into the difference between surface grain behavior and interior grain behavior. Developing models that realistically predict grain to grain heterogeneity and verifying those models is a basic element in modeling mechanical behavior. Heterogeneity is particularly important to fatigue in which the most unfavorably oriented grain is the site of failure.

Keywords: Micromechanical, Viscoplasticity, Grain Boundary, Crystallographic Slip, High Temperature, Experiments

145. **MICROMECHANICAL VISCOPLASTIC STRESS-STRAIN MODEL WITH GRAIN BOUNDARY SLIDING**
$0
DOE Contact: Oscar P. Manley, (301) 903-5822
Engineering Science Software, Inc., Contact: K. P. Walker, (401) 231-3182

This project is joint with the University of Connecticut project described above. See the previous paragraph for a description.

Keywords: Micromechanical, Viscoplasticity, Grain Boundary, Crystallographic Slip, High Temperature, Constitutive Model

146. **AN ANALYTICAL-NUMERICAL ALTERNATING METHOD FOR 3-D INELASTIC FRACTURE AND INTEGRITY ANALYSIS OF PRESSURE-VESSELS AND PIPING AT ELEVATED TEMPERATURES**
$61,325
DOE Contact: Oscar P. Manley, (301) 9903-5822
Georgia Institute of Technology Contact: S. Atluri, (404) 894-2758

This research effort involves the application of highly efficient and accurate analytical-numerical alternating methods for the non-linear analysis of surface-flawed pressure vessels and piping under (1) elastic-plastic fracture, (2) high-temperature creep and viscoplastic fracture, and (3) pressurized thermal shock conditions. These procedures are highly efficient because only the uncracked structure is modeled numerically (finite element and boundary element approaches) and the severity of the stress state due to the presence of the 3-dimensional flaw is accounted for entirely analytically. This procedure is a novel application of the Schwartz-Neumann alternating method, which is a superposition method for linear problems, being extended to the nonlinear problems of elastoplasticity and creep through the generalized mid-point radial return mapping procedures which return the elastic estimates of stress in the cracked body to the appropriate yield surface. This effort is being conducted in collaboration with researchers at the University of Washington where some seminal experimental work is being conducted to verify and validate the analytical work done at Georgia Tech.

Keywords: Fracture, Failure Analysis

147. **IN-FLIGHT MEASUREMENT OF THE TEMPERATURE OF SMALL, HIGH VELOCITY PARTICLES**
$436,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Idaho National Engineering Laboratory Contact:
J. R. Fincke, (208) 526-2031

The measurement of temperature, velocity, enthalpy, and species concentration in high temperature gases such as weakly ionized thermal plasmas has considerable importance in the areas of plasma thermal spray and the thermal plasma synthesis of materials. In particular, the dynamics of the plasma, the interaction of the plasma with its surroundings and the behavior of particles immersed in the plasma surrounding it are important in the understanding, development and optimization of plasma process that involve fine powders. Laser based measurement techniques have been developed at this laboratory and are being applied to the study of thermal plasmas. In addition to the laser techniques enthalpy probes coupled to a mass spectrometer also provide temperature, velocity and concentration information. The experimental data produced is used to benchmark the modeling work done under a related program in "Modeling of Thermal Plasma Processes" (see J. Ramshaw, INEL).

Keywords: Plasma Processing, Particle/Plasma Interaction

148. **INTELLIGENT CONTROL OF THERMAL PROCESSES**
$224,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Idaho National Engineering Laboratory Contacts:
H. B. Smartt, (208) 526-8333 and J. A. Johnson, (208) 526-9021

This project addresses intelligent control of thermal processes as applied to materials processing. Intelligent control is defined as the combined application of process modeling, sensing, artificial intelligence, and control theory to process control. The intent of intelligent control is to produce a good product without relying on post-process inspection and statistical quality control procedures. The gas metal arc welding process is used as a model system; considerable fundamental information on the process has been developed at INEL and MIT during the past six years. Research is being conducted on an extension of the fundamental process physics, application of neural network-like dynamic controllers and signal/image processors, and development of noncontact sensing techniques.

Tasks include physics of nonlinear aspects of molten metal droplet formation, transfer, and substrate thermal interaction; understanding substrate thermal interaction; understanding the relationship of neural network structure and associated learning algorithm to model development and learning dynamics in neural networks with the objective of obtaining a fundamental understanding of network transfer functions; and advanced sensing, including the propagation and interaction of ultrasound in metallic solid and liquid media.

Keywords: Welding, Ultrasonic Sensing, Optical Sensing

149. **ELASTIC-PLASTIC FRACTURE ANALYSIS EMPHASIS ON SURFACE FLAWS**
$687,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Idaho National Engineering Laboratory Contact:
W. G. Reuter, (205) 526-0111

The objective is to improve design and analytical techniques for predicting the integrity of flawed structural components. The research is primarily experimental, with analytical evaluation guiding the direction of experimental testing. Tests are being conducted on a material (a modified ASTM A-710) exhibiting a range of fracture toughness but essentially constant yield and ultimate tensile strength. As test temperature increases, the specimen configuration-fracture toughness relationship complies initially with requirements for linear elastic-fracture mechanics and extends beyond the range of a J-controlled field. Presently, compact tension and bend specimens are being used to develop state-of-the-art fracture mechanics.

Metallographic techniques are being used to measure crack tip opening displacement and remaining ligament size for comparison with analytical models. Other techniques including microphotography and the replicating of the crack tip region, for future metallographic examination, are being used to complement the above measurements to identify limits and capabilities of each technique. Moire interferometry techniques are being used to evaluate and quantify the deformation in the crack region. These data are being used to experimentally measure J and CTOD for standard (CT and SENB) specimens as well as for specimens containing surface cracks.

The above tests have been supplemented by using specimens fabricated from aluminum (dimple rupture only) and titanium. The titanium specimens are being used to study the fracture behavior and the ability of existing models to predict failure for weldments. Moire interferometry techniques are being used to study the local constitutive behavior and the fracture process at the crack tip region of the weldment.

Keywords: Fracture, Metals: Ferrous

150. **MODELING OF THERMAL PLASMA PROCESSES**
$210,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Idaho National Engineering Laboratory Contacts:
J. D. Ramshaw, (208) 526-9240 and
C. H. Chang, (208) 526-2886

Optimization of thermal plasma processing techniques requires a better understanding of the space- and time-resolved flow and temperature distributions in the plasma plume and of the interaction between the plasma and a particulate phase. This research is directed toward the development of a comprehensive computational model of thermal plasma processes and plasma-particle interactions capable of providing such information. The model is embodied in the LAVA computer code for two- or three-dimensional transient or steady state thermal plasma simulations. LAVA uses a rectangular mesh with an excluded volume function to represent geometrical obstructions and volume displaced by particles. Simple highly vectorizable numerics are utilized, with rapid steady state and low-speed flow options. The plasma is represented as a multicomponent fluid governed by the transient compressible Navier-Stokes equations. Real gas physics is allowed for by temperature-dependent specific heats and transport properties. Multicomponent diffusion is calculated in a self-consistent effective binary diffusion approximation, including ambipolar diffusion of charged species. Both k-epsilon and subgrid-scale turbulence models are included. Dissociation, ionization, and plasma chemistry are represented by means of general kinetic and equilibrium chemistry routines. Discrete particles interacting with the plasma will be represented by a stochastic particle model similar to that previously used to model liquid sprays. This model allows for spectra of particle sizes, shapes, temperatures, etc., thereby capturing the important statistical aspects of the problem. It will include sub-models for the various plasma-particle and particle-particle interaction processes, including melting, evaporation, condensation, nucleation, agglomeration, and coalescence.

Keywords: Plasma Processing, Optimization, Computational Model

151. **NONDESTRUCTIVE EVALUATION OF SUPERCONDUCTORS**
$180,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Idaho National Engineering Laboratory Contact:
K. L. Telschow, (208) 526-1264

The purpose of this task is to perform fundamental research which will lead to the development and application of new nondestructive evaluation (NDE) techniques and devices for the characterization of high-temperature superconducting materials. In the near future, application of these new superconductors will require NDE methods for evaluating the properties of wires, tapes and coatings. Microstructural and, particularly, superconducting properties must be measured noninvasively in a manner capable of providing spatial information so that fabrication processes can be optimized. Although the fabrication of these ceramic materials is being pursued by many different techniques at present, there is enough similarity in the different superconducting materials and the fabricated forms to begin research into NDE measurement techniques. In FY89 this project began identifying techniques that can determine critical superconducting properties on a local scale. This has resulted in the use of AC induced currents in conjunction with DC transport currents to determine critical currents and dissipation locally. The analysis of these measurements is being carried out with the aid of the London and "Critical State" models for supercurrent flow in these materials. These results are being correlated with material microstructure information and other measurement techniques.

Keywords: NDE, Superconductors

152. **STRESS INDUCED PHASE TRANSFORMATIONS**
$67,419
DOE Contact: Oscar P. Manley, (301) 903-5822
University of Illinois Contact: H. Sehitoglu,
(217) 333-4112

Understanding stress-induced phase transformations is of paramount importance in modeling the behavior of engineering materials and components. From the material behavior standpoint, transformations generate internal (micro) stresses which alter the constitutive behavior, and from the component standpoint transformation strains may result in dimensional changes and alteration of macroscopic stress fields. The transformation strains are strong functions of the applied stress state since favorably oriented planes transform in the course of loading. Several unique experiments under combined shear stress-hydrostatic pressure are conducted on steels, containing retained austenite, in order to measure and study anisotropic transformation strains. Test specimens are subjected to externally applied pressures in excess of 700 MPa. The compressive hydrostatic stresses would increase the extrinsic ductility of the material, and hence permit high magnitudes of the stress-induced and strain-induced transformations. Based on these experiments, the work will set the background to evaluate the theories proposed, and lay the foundation for new ones with particular emphasis on complex changes in transformation strains. The basic information obtained from the work will generate improved understanding of transformation under contact loadings and transformation toughening phenomenon in metallic and non-metallic materials.

Keywords: Phase Transformation, Stress, Strain

153. **PULSE PROPAGATION IN INHOMOGENEOUS OPTICAL WAVEGUIDES**
$0
DOE Contact: Oscar P. Manley, (301) 903-5822
University of Maryland Contact: C. Menyuk, (301) 455-3501

Our research, which was originally focused on light propagation in inhomogeneous optical fibers, has broadened in scope to include studies of solid state rib waveguides and Y-junctions which are used to guide and switch light. The work on optical fibers is divided into two research projects.

The first project concerns long-distance communication using solutions. We have been particular concerned with the effects of randomly varying birefringence, and we have shown that its effect is benign. From the basic equations we were able to show from an appropriate ordering expansion that the nonlinear Schrodinger equation is the lowest order equation and, hence, we expect its behavior to dominate the soliton evolution even in a highly birefringent fiber, as long as the birefringence is rapidly varying. We have also studied optical fiber soliton switches based on trapping and dragging. To do the work on optical fibers, we have collaborated with scientists at AT&T Bell Laboratories. The first solid state project was to find the effect of a quantum well on the propagation characteristics of a rib waveguide. Using a planar guide as reference, we were able to show that the effect of the real geometry is qualitatively small but can have a significant quantitative effect.

The second solid-state project is to determine the effect of dry-etching on the mode-holding characteristics of the device. As a consequence of the etching, the height at which the junction splits can vary. We showed that the rounding has a very small effect, in contrast to blunting which occurs when the materials are chemically wet etched.

Keywords: Optical Fibers, Pulse Propagation, Inhomogeneities, Imperfections

154. **MULTIVARIABLE CONTROL OF THE GAS-METAL/ARC WELDING PROCESS**
$152,609
DOE Contact: Oscar P. Manley, (301) 903-5822
MIT Contact: David E. Hardt, (617) 253-2429

The Gas-Metal Arc Welding Process (GMAW) is a highly productive means for joining metals and is being used increasingly for structures and pressure vessels. The overall objective of this work is to examine the problem of simultaneous regulation of all real-time attributes of a weld. Past work has established the viability of independent control of thermal characteristics and the present work is examining the geometric aspects of weld pool control.

One objective of this work is to develop basic process modeling and control schemes to allow independent regulation of the weld bead width and height. A control model relating wirefeed and travel speed to width and height was developed using transfer function identification techniques applied to a series of step welding tests. We are developing a control system to independently regulate the weld bead width and the width of the heat affected zone. Initial work is concentrating on simulation of wide seam welding using an analytical heat transfer model as well as a finite difference process model. A key issue in the problem is the strong coupling between the inputs (current and travel speed) and the outputs. The use of high frequency transverse motion of the torch is being investigated as a means of overcoming this coupling. Once the control latitude is increased, a two variable control scheme based on both video and infrared sensing will be implemented.

Finally, the depth of penetration of a weld is the most important indicator of weld strength, yet it is the one variable that is essentially impossible to measure directly. A real-time depth estimator has been developed based on solution of an inverse heat transfer problem. Surface temperature measurements from the top and bottom of the weld have shown accurate and rapid convergence and development of a depth control system based on this estimator is now being processed.

This project is a collaborative program with INEL.

Keywords: Welding, Control

155. **METAL TRANSFER IN GAS-METAL ARC WELDING**
$123,688
DOE Contact: Oscar P. Manley, (301) 903-5822
MIT Contacts: T. W. Eagar and J. Lang, (617) 253-3229

The present research is part of a cooperative program among faculty at MIT and staff at the Idaho National Engineering Laboratory (INEL) to develop a sound understanding of the arc welding process and to develop sensing and control methods that can be used to automate the gas-metal arc process.

The research during the current year has reviewed methods of filtering the voltage and current waveforms during pulsed current welding in order to extract signals which can be used to control the process. A new process control system has been developed and integrated with the welding equipment. Work has begun to study methods of mechanically controlling droplet detachment from the welding electrode.

Keywords: Welding, Control

156. **MODELING AND ANALYSIS OF SURFACE CRACKS**
$191,628
DOE Contact: Oscar P. Manley, (301) 903-5822
MIT Contacts: David M. Parks, (617) 253-0033 and F. A. McClintock, (617) 253-2219

This research focuses on the analysis of ductile crack initiation, growth and instability in part-through surface-cracked plates and shells. The overall approach consists of careful calculations of crack front stress and deformation fields, and correlation of cracking with experimental observations being conducted at the Idaho National Engineering Laboratory. Recently, significant progress has been achieved in developing and applying a two-parameter description of crack front fields.

Simplified engineering applications of surface crack analysis are being developed in the context of the line-spring model. Specific enhancements include improved elastic-plastic procedures for the practically important case of shallow surface cracks, as well as simple methods for calculating the T-stress along surface cracks fronts.

Detailed elastic-plastic stress analyses of cracked structural geometries provide a basis for interpreting experimental observations, for quantitatively assessing inherent limitations of nonlinear fracture mechanics methodology, and for extending these boundaries through development of two-parameter characterization of crack tip fields. Simplified but accurate analytical methods are also under development for analysis of surface-cracked plates and shells. Emphasis is placed on better understanding complex three-dimensional features of elastic-plastic crack tip fields.

Keywords: Fracture

157. **THERMAL PLASMA PROCESSING OF MATERIALS**
$0
DOE Contact: Oscar P. Manley, (301) 903-5822
University of Minnesota Contact: E. Pfender, (612) 625-6012

The objective of this research project is to study analytically and experimentally specific thermal plasma processes for materials treatment. Processes of interest include the synthesis of ultrafine ceramic powders and of films.

During the past year our efforts have concentrated on characterizing the thermal plasma chemical vapor deposition (TPCVD) process of diamond films onto various substrates. Modeling of the situation close to the substrate indicates extremely steep temperature and concentration gradients pointing to the important of thermal diffusion.

Very high diamond deposition rates up to 1 mm/hr have been observed with a plasma reactor with recirculation eddies. A series of diagnostic studies have been initiated to facilitate an understanding of the main reasons for the observed high deposition rates.

Keywords: Plasma Processing, Plasma Diagnostics

158. **DEVELOPMENT OF MEASUREMENT CAPABILITIES FOR THE THERMOPHYSICAL PROPERTIES OF ENERGY-RELATED FLUIDS**
$416,000
DOE Contact: Oscar P. Manley, (301) 903-5822
National Institute of Standards and Technology Contacts: R. Kayser, (301) 975-2483 and J. M. H. Sengers, (301) 975-2463

The major objective of this project is to develop state-of-the-art experimental apparatus that can be used to measure the thermophysical properties of a wide range of fluids and fluid mixtures important to the energy, chemical, and energy-related industries and to carry out carefully selected benchmark measurements on key systems. The research is being done jointly by two groups within the Thermophysics Division of the NIST Chemical Science and Technology Laboratory; one group is located in the Gaithersburg, MD, laboratories and the other at the Boulder laboratories. The specific measurement capabilities to be developed in this project include new apparatus for transport properties (thermal conductivity and viscosity), for thermodynamic properties (pressure-volume-temperature data and enthalpy), for phase equilibria properties (vapor-liquid equilibria, coexisting densities, and dilute solutions), and for dielectric properties (dielectric constant). These new apparatus will extend significantly the existing state of the art for properties measurements and make it possible to study a wide range of complex fluid systems (e.g., highly polar, electrically conducting, and reactive fluids) under conditions which have been previously inaccessible. This project also includes benchmark experimental measurements on systems containing alternative refrigerants, on aqueous solutions, and on carefully selected systems with species of diverse size and polarity that are important to the development of predictive models for energy-related fluids.

Keywords: Thermophysical Properties, Mixtures, Fluids, High Temperature, High Pressure

159. **LOW RESISTIVITY OHMIC CONTACTS BETWEEN SEMICONDUCTORS AND HIGH-T_c SUPER-CONDUCTORS**
$86,000
DOE Contact: Oscar P. Manley, (301) 903-5822
National Institute of Standards and Technology Contacts: J. Moreland, (303) 497-3641 and J. W. Ekin, (303) 497-5448

The purpose of this project is to fabricate and characterize high-T_c superconductor/semiconductor contacts. Developing a method for optimizing the current capacity of such contact will extend the application of high-T_c superconductors to hybrid superconductor/semiconductor technologies. These technologies include integrated circuit interconnects (both on-chip and package) and proximity superconductor/semiconductor/superconductor SNS Josephson junctions. Presently, these are among the most promising high-T_c superconductor applications, but an essential first step is the development of reliable, stable, ohmic contacts between semiconductors and the high-T_c oxide superconductors.

The initial phase of this program is to determine the compatibility of various metals and alloys (Au and Al alloys and W, for example) as contact materials for superconducting YBCO and other high T_c materials. Once a good combination has been established, patterned YBCO/normal metal contacts will be deposited onto semiconductor wafer surfaces. We have purchased a sputter co-deposition system for YBCO thin films and have adapted three other vacuum systems for contact deposition including two sputtering systems and an evaporator.

Keywords: High-Tc Superconductors, Semiconductors, Contact, Low Resistivity

160. **THIN FILM CHARACTERIZATION AND FLAW DETECTION**
$91,537
DOE Contact: Oscar P. Manley, (301) 903-5822
Northwestern University Contact: J. D. Achenbach, (312) 491-5527

The work on this project is concerned with applications of the scattered field approach to the detection and characterization of cracklike flaws. The work is both analytical and numerical in nature.

The efficacy of ultrasonic methods to detect and characterize a crack depends on topographical features of the crack faces, the presence of inhomogeneities in the crack's environment, and on the mechanical properties in the near-crack region. In this work the effects on the scattered ultrasonic field of various features of fatigue and stress corrosion cracks, such as partial crack closure, the presence of microcracks and microvoids, and near-tip zones of different mechanical properties have been investigated. Most of the results have been obtained by formulating a set of singular integral equations for the fields on the boundaries of the scattering obstacles. These equations have been solved numerically by the boundary element method, and the scattered fields have subsequently been obtained by using representation integrals.

For the configurations examined in this work, crack closure has the most significant effect on far-field scattering.

Keywords: Non-Destructive Evaluation, Superconductors, Scattering

161. **EXPERIMENTS ON THE GAS DYNAMICS OF THE HIGH VELOCITY OXY-FUEL (HVOF) THERMAL SPRAY PROCESS**
$94,981
DOE Contact: Oscar P. Manley, (301) 903-5822
Pennsylvania State University Contact: G. Settles, (814) 863-1504

This reseach program involves an experimental study of the gas dynamics of high-velocity oxy-fuel (HVOF) thermal sprays, a promising new technology in the fields of materials, manufacturing, and the extension of the useful life of large equipment. HVOF relies on combustion to melt and propel solid particles at high speeds onto a surface to be coated. The principles of gas dynamics govern the expansion of this gas/particle stream from high stagnation conditions to produce a supersonic jet. The current scientific basis of the HVOF process is poorly understood; dramatic improvements in the HVOF thermal spray are likely by applying the principles of gas dynamics which is a well-developed field in the disciplines of high-speed aerodynamics and propulsion. The specific approach is to use a properly-shaped nozzle and an appropriate pressure ratio to demonstrate that a perfectly-expanded supersonic jet constitutes the central physical principle upon which the HVOF thermal spray can be based. In such case the temperature-time history of the sprayed particles can be tailored to achieve coatings with specific properties, and to minimize oxidation due to mixing with the surrounding air.

Keywords: Surface Coatings, HVOF Sprays

162. **TRANSPORT PROPERTIES OF DISORDERED POROUS MEDIA FROM THE MICROSTRUCTURE**
$101,185
DOE Contact: Oscar P. Manley, (301) 903-5822
Princeton University Contact: S. Torquato, (609) 258-4600

This research program is concerned with the quantitative relationship between transport properties of a disordered heterogeneous medium that arise in various energy-related problems (e.g., thermal or electrical conductivity, trapping rate, and the fluid permeability) and its microstructure. Attention will be focused on studying the effect of porosity, spatial distribution of the phase elements, interfacial surface statistics, anisotropy, and size distribution of the phase elements, on the effective properties of models of both unconsolidated media (e.g., soils and packed beds of discrete particles) and consolidated media (e.g., sandstones and sintered materials).

Both theoretical and computer-simulation techniques have been employed to quantitatively characterize the microstructure and compute the transport properties of disordered media.

Keywords: Disordered Media

163. **EFFECT OF FORCED AND NATURAL CONVECTION ON SOLIDIFICATION OF BINARY MIXTURES**
$103,571
DOE Contact: Oscar P. Manley, (301) 903-5822
Purdue University Contact: F. Incropera, (317) 494-5688

This study deals with the influence of combined convection mechanisms on the solidification of binary systems. A major accomplishment of research performed to date has been the development and numerical solution of a continuum model, which uses a single set of equations to predict transport phenomena in the liquid, "mushy" (two-phase), and solid regions of the mixture. Calculations have been performed for two-dimensional, aqueous salt solutions involving forced convection, thermo/solutal natural convection, and/or thermo/diffusocapillary convection. The calculations have revealed a wide variety or rich and robust flow conditions, including important physical features of the solidification process which have been observed experimentally but have heretofore eluded prediction. These features include double-diffusive layering in the melt, development of an irregular liquidus front, remelting of solid, development of flow channels in the mushy region, and the establishment of characteristic macrosegregation patterns (regions of significantly different composition) in the final solid.

The primary objective of current studies is to determine the manner in which externally imposed forces influence thermo-solutal convection in the mushy and liquid regions during solidification of a binary mixture. A special goal is to determine means by which the forces may be used to offset or dampen thermo/solutal convection, thereby reducing macrosegregation and attendant casting defects. Separate consideration is being given to the effects of magnetic and centrifugal forces on solidification in binary metallic alloys and aqueous salt solutions, respectively. Predictions based on the continuum model are being compared with measurements obtained for metallic (Pb-Sn) and aqueous (NH_4Cl-H_2O) systems.

Keywords: Solidification, Convection, Binary Alloys, Salt Solutions, Magnetic Fields, Centrifugal Forces

164. **INELASTIC DEFORMATION AND DAMAGE AT HIGH TEMPERATURE**
$0
DOE Contact: Oscar P. Manley, (301) 903-5822
Rensselaer Polytechnic Institute Contact: Erhard Krempl, (518) 266-6432

A combined theoretical and experimental investigation is performed to study the biaxial deformation and failure behavior of engineering alloys under low-cycle fatigue conditions at elevated temperature. The purpose is to characterize the material behavior in mathematical equations which are ultimately intended for use in inelastic stress analysis and life prediction. Creep-fatigue interaction and ratchetting are of special concern. The long-term goal is the development of a finite element program that can directly calculate the life-to-crack initiation of a component under a given load history.

Keywords: Fracture, Damage

165. **FLUX FLOW, PINNING AND RESISTIVE BEHAVIOR IN SUPERCONDUCTING NETWORKS**
$70,519
DOE Contact: Oscar P. Manley, (301) 903-5822
University of Rochester Contact: S. Teitel, (716) 275-4039

The motion of vortex structures, in response to applied currents, is a major source of resistance in superconducting networks in magnetic fields. Systems of interest include regular Josephson junction arrays and type II superconductors, such as the new granular high T_c ceramics. Numerical simulations of finite temperature, current carrying networks will be carried out to provide a characterization of vortex response in non-equilibrium situations. For periodic networks, current-voltage (I-V) characteristics will be computed and compared with experimental results. The effects on resistivity of transitions from pinned to unpinned or to melted vortex structures, will be investigated. For disordered networks, the effects of pinning in producing metastable vortex structures leading to glassy behavior will be explored.

To date, simulations have been carried out for the "fully frustrated" two dimensional regular Josephson junction array. I-V characteristics were computed and reasonable agreement found with experiment. Behavior was explained within a simple physical model, in which correlations between vortices is crucial for producing the critical excitations leading to vortex flow resistance.

Keywords: Flux Flow, Pinning, Vortex Motion, Superconductors

166. **STABILITY AND STRESS ANALYSIS OF SURFACE MORPHOLOGY OF ELASTIC AND PIEZOELECTRIC MATERIALS**
$135,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Stanford University Contact: H. Gao, (415) 725-2560

The goal of this research is to investigate the mechanical effects of surface morphology of elastic dielectric and piezoelectric materials. In particular, the project will study the stability of a flat surface against diffusional perturbations and the stress concentration caused by slightly undulating surfaces.

The surface morphology of materials will be studied by using a unified perturbation procedure based on the notion of thermodynamic forces and the energy momentum tensor. The thermodynamic forces on material inhomogeneities such as interfaces and inclusions are a measure of the rate at which the total energy of a physical system varies with the configurational change of these inhomogeneities. Within the general methodology, any type of material and loading condition can be studied as long as the proper forces can be identified. By using corresponding material conservation laws discovered previously, a systematic analysis of surfaces of piezoelectric solids will be made. Preliminary studies have shown that under sufficiently large stresses, surfaces of materials become unstable against a range of diffusional perturbations bounded by two critical wave lengths. Even a slight undulation caused by these unstable diffusional perturbations, such as micro-level bumps and troughs, can result in a significant stress concentration along a material surface. These concentrations may lead to mechanical failures along the surface and may have more consequences for piezoelectric materials where the deformation is coupled to an applied electric field. There are also suggestions that the stress distributions in a body may be sensitive to the surface morphology.

Keywords: Stress Analysis, Surface Morphology, Elastic, Dielectric, Piezoelectric Materials

167. **OPTICAL TECHNIQUES FOR SUPERCONDUCTOR CHARACTERIZATION**
$145,000
DOE Contact: Oscar P. Manley, (301) 903-5822
Stanford University: G. S. Kino, (415) 497-0205

The aim of this project is to develop a photothermal microscope for noncontact testing of materials. Techniques of this kind are particularly well suited to the determination of thermal parameters, and anisotropy of small samples.

One example of the work is the measurement of high temperature superconductors over a range of temperatures from room temperature through the critical temperature T_c down to 20°K. A modulated laser beam, focused to less than 1 m diameter, impinges through a sapphire window onto a sample of Bi-Ca-Sr-Cu-O in a helium cryostat and periodically modulates its temperature. This process excites a thermal wave, which can be detected by the variation in reflected signal amplitude of a second focused laser beam, due to the change of refractivity with temperature. The sample can be rotated under the beams and the thermal diffusion coefficient, its anisotropy and its magnitude can be measured from the phase delay of the thermal wave. By measuring the amplitude of the thermal wave, material phase changes associated with superconductivity can be measured. A pronounced peak in amplitude is seen at the critical temperature T_c. Even stronger effects of this type are observed with charge density waves in a variety of materials.

Keywords: Nondestructive Evaluation, Acoustic Sensors

168. **DEGENERATE FOUR-WAVE MIXING AS A DIAGNOSTIC OF PLASMA CHEMISTRY**
$0
DOE Contact: Oscar P. Manley, (301) 903-5822
Stanford University Contact: R. Zare, (415) 723-3062

A need exists for *in situ* nonintrusive diagnostics for probing trace and highly reactive radical intermediates in nonequilibrium plasma used for chemical vapor deposition. We propose applying a novel nonlinear spectroscopic technique, degenerate four-wave mixing (DFWM). The DFWM signal is a coherent scattered beam at frequency which is generated by the nonlinear response of the medium to the interaction of three incident waves at the same frequency. The signal is enhanced by a resonant transition and offers a form of Doppler-free spectroscopy with extremely high spectral, spatial, and temporal resolution. Signal detection is remote and does not suffer from background interference from the bright plasma source. In addition, the phase conjugate nature of the signal eliminates optical aberration. The environment we propose to study is an atmospheric-pressure rf-inducively-coupled plasma and the target radicals include CH, CH_2, C_2, C_2H, and CH_3 that are important in plasma synthesis of diamond thin films. The spatial sensitivity of DFWM will be used to study the coupling of gas-phase and gas-surface chemistry by measuring temperature and concentration profiles. The proposed research will advance diagnostic techniques for plasma environments and provide a better understanding of the plasma chemistry of diamond synthesis.

Keywords: Plasma, Four-Wave Mixing

169. **EFFECTIVE ELASTIC PROPERTIES AND CONSTITUTIVE EQUATIONS FOR BRITTLE SOLIDS UNDER COMPRESSION**
$0
DOE Contact: Oscar P. Manley, (301) 903-5822
Tufts University Contact: Mark Kachanov, (617) 628-5000, ext. 2821

The knowledge of effective elastic properties of solids with cracks appears to be of increasing engineering importance. Extensive microcracking in structural elements working under conditions of high temperatures or irradiation, microcracking in composite materials under fatigue conditions may noticeably reduce the stiffness of the material and make it anisotropic. Understanding and prediction of these changes are essential for proper design and strength and lifetime assessments.

A new approach to many crack problems based on interrelating the average tractions on individual cracks is introduced. Its advantages are that it yields simple analytical results which are quite accurate up to very high crack densities and that it can be applied to crack arrays or arbitrary geometry. Relation between deterioration of elastic properties and "damage" is discussed.

Keywords: Fracture, Elasticity

170. **3-D EXPERIMENTAL FRACTURE ANALYSIS AT HIGH TEMPERATURE**
$69,975
DOE Contact: Oscar P. Manley, (301) 903-5822
University of Washington Contact: Albert Kobayashi, (206) 543-5488

This research deals with a detailed experimental investigation of the nonlinear deformation and failure of surface-flawed pressure vessels and piping. It includes (1) elastic-plastic fracture, and (2) high-temperature creep and viscoplastic fracture. The objective of this effort is to acquire an understanding of the mechanics of the initial phases of failure and, thereby, provide better designs and life assessments of critical structural parts. This effort is being conducted in collaboration with Georgia Institute of Technology which is performing the theoretical research of the overall and crack-tip fields.

Keywords: Fracture, Failure Analysis

171. **SIMULATION AND ANALYSIS OF DYNAMIC FAILURE IN DUCTILE MATERIALS**
$98,919
DOE Contact: Oscar P. Manley, (301) 903-5822
Brown University Contact: B. Freund, (401) 863-1157

This mainly theoretical effort is a part of a joint program with the California Institute of Technology, where Professor Rozakis, under a separate grant, contributes the necessary data obtained by novel measurement techniques.

Dynamic crack initiation and growth in ductile metals is still poorly understood, in spite of the fact that many energy structures are built using such materials. Unlike static considerations of crack propagation in brittle materials, the corresponding dynamical crack evolution is intrinsically three dimensional and, until recently, beyond experimental and computational capabilities. Recent advances reported in the literature have shown the feasibility of carrying out the proposed research with existing or readily accessible resources.

The specific objectives of this project include: study of the plain strain deformation of a thick-walled cylinder subjected to suddenly applied pressure or equivalent loading; detailed examination and modeling of a ductile failure process including three dimensional effects as exhibited in the data to be obtained by Professor Rosakis at Caltech; the interaction of dynamically growing cracks in ductile materials, leading up to structural failure under intense loading conditions.

Keywords: Fracture, Ductility, Dynamic

172. **DYNAMIC FAILURE CHARACTERIZATION OF DUCTILE STEELS**
$99,664
DOE Contact: Oscar P. Manley, (301) 903-5822
California Institute of Technology Contact: A. Rozakis, (818) 395-4523

This mainly experimental effort is a part of a joint program with Brown University, where Professor B. Freund contributes his theory and modeling efforts.

Dynamic crack initiation and growth in ductile metals is still poorly understood, in spite of the fact that many energy structures are built using such materials. Unlike static considerations of crack propagation in brittle materials, the corresponding dynamical crack evolution is intrinsically three dimensional and, until recently, beyond experimental and computational capabilities. Recent advances reported in the literature have shown the feasibility of carrying out the proposed research with existing or readily accessible resources.

The specific objectives of this project include: damage models for deformation of stainless steels as a function of strain, strain rate and temperature; novel optical and IR techniques for observing crack initiation and evolution under a range of loading rates; 3-D aspects of crack initiation; determination of the criteria for crack initiation, growth and arrest; numerical simulation of dynamic failure experiments including thermomechanics of damage evolution.

Keywords: Fracture, Ductility, Dynamic

GEOSCIENCES RESEARCH

The BES Geosciences Research Program supports research that is fundamental in nature and of long-term relevance to one or more energy technologies, national security, energy conservation, or the safety objectives of the Department of Energy. It is also concerned with the extraction and utilization of such resources in an environmentally acceptable way. The purpose of this program is to develop geoscience or geosciences-related information relevant to one or more of these Department of Energy objectives or to develop the broad, basic understanding of geologic materials and processes necessary for the attainment of long-term Department of Energy goals. In general, individual research efforts supported by this program may involve elements of several different energy objectives. The DOE contact for this Program is William C. Luth, (301) 903-5822.

MATERIALS PREPARATION, SYNTHESIS, DEPOSITION, GROWTH OR FORMING

173. **AN INVESTIGATION OF ORGANIC ANION-MINERAL SURFACE INTERACTIONS DURING DIAGENESIS**
$199,500
DOE Contact: W. C. Luth, (301) 903-5822
SNL Contacts: Patrick Brady, (505) 844-7216 and Randall Cygan, (505) 844-7216

The research is to investigate adsorption of anionic carboxylate and phenolate groups onto aluminosilicate surfaces in order to evaluate the role of organic acids as (1) catalysts for mineral dissolution and porosity evolution in deep basins, and (2) controlling agents of coupled dissolution and growth of during diagenesis. Combined experimental and theoretical approaches are used to investigate the mechanisms and reaction rates of organic anion adsorption. T-dependent adsorption of oxalate, acetate, salicylate and benzoate anions onto selected aluminosilicate surfaces are being measured, as are dissolution rates of alumina (as corundum), tremolite, albite, kaolinite and precipitation rates of kaolinite, in solutions containing various organic acids, at temperatures of 30-90°C. Theoretical investigations are testing mechanistic connections between metal-anion complexation, anion adsorption, and mineral growth with the new experimental data. The influence of surface-site chemistry and bonding are being investigated, in an attempt to establish general crystal-chemical rules for predicting the extent of organically-controlled reactions during diagenesis.

Key Words: Surface Reactions, Aluminosilicate Minerals, Adsorption Mechanisms

174. **TRANSITION METAL CATALYSIS IN THE GENERATION OF PETROLEUM AND NATURAL GAS**
$136,179
DOE Contact: W. C. Luth, (301) 903-5822
Rice University Contact: Frank D. Mango, (713) 527-4880

Light hydrocarbons in petroleum, including natural gas (C_1-C_4), are conventionally viewed as products of progressive thermal breakdown of kerogen and oil. Alternatively, transition metals, activated under the reducing conditions of diagenesis, can be proposed as catalysts in the generation of light hydrocarbons. Transition metal-rich kerogenous sedimentary rocks were reacted under reducing conditions at temperatures for which the substrates alone, *N*-octadecene + hydrogen, are stable indefinitely. Catalytic activity was measured to be on the order of 10^{-7} g CH_4/d/g kerogen, suggesting robust catalytic activity over geologic time at moderate sedimentary temperatures.

Keywords: Transition Metals, Catalysis, Petroleum

MATERIALS STRUCTURE AND COMPOSITION

175. **REACTION MECHANISMS OF CLAY MINERALS AND ORGANIC DIAGENESIS: AN HRTEM/AEM STUDY**
$125,696
DOE Contact: W. C. Luth, (301) 903-5822
Arizona State University Contact: P. R. Buseck, (602) 965-3945

The research is to investigate the structures of fine-scale diagenetic material using high-resolution transmission electron microscopy/analytical electron microprobe (HRTEM/AEM) techniques which will facilitate *in situ* identification and evaluation of reaction mechanisms. As a basis for kinetic models this information is used to predict basinal diagenetic patterns for resource exploration. Structural analyses of intergrown product and reactant from three principal diagenetic reactions operative in the formation of hydrocarbon reservoirs are proposed: (1) berthierine to chamosite, (2) smectite to illite, and (3) maturation of kerogen to form oil and gas.

Keywords: Diagenetic Reactions, High-Resolution Transmission Electron Microscopy, Kerogen, Smectite, Illite, Berthierine, Chamosite

176. **INFRARED SPECTROSCOPY AND HYDROGEN ISOTOPE GEOCHEMISTRY OF HYDROUS SILICATE GLASSES**
$123,000
DOE Contact: W. C. Luth, (301) 903-5822
Caltech Contacts: S. Epstein, (818) 356-6100 and E. Stolper, (818) 356-6504

The focus of this project is the combined application of infrared (IR) spectroscopy and stable isotope geochemistry to the study of dissolved components in silicate melts and glasses. Different species of dissolved water and carbon dioxide (e.g., molecules of H_2O and hydroxyl groups, molecules of CO_2 and carbonate ion complexes) have been analyzed to understand volatile transfer reactions in liquids and glasses. The partitioning of H isotopes between vapor and hydroxyl groups and molecules of H_2O dissolved in rhyolitic melts was measured. Concentrations of H_2O and CO_2 in volcanic glasses and CO_2 in rhyolitic liquid were measured at pressures up to 1500 bars. The fractionation of O isotopes between CO_2 vapor and rhyolitic glass and melt was measured. The kinetics of OH-forming reactions in silicate glasses were studied. Diffusion of water in basaltic melts and of water and CO_2 in rhyolitic glasses and melts was studied. Results were used to understand oxygen "self-diffusion" in silicate minerals and glasses and enhanced oxygen diffusion under hydrothermal conditions.

Keywords: Infrared Spectroscopy, Silicate Minerals, Glasses, Silicate Liquids, Speciation

177. **BIOMINERALIZATION: SYSTEMATICS OF ORGANIC-DIRECTED CONTROLS ON CARBONATE GROWTH MORPHOLOGIES AND KINETICS DETERMINED BY *IN SITU* ATOMIC FORCE MICROSCOPY**
$90,891
DOE Contact: W. C. Luth, (301) 903-5822
Georgia Inst. of Technology Contact: P. Dove, (404) 894-6043

The research is to investigate biomineralization mechanisms of dissolution and precipitation reactions of the two common calcium carbonate polymorphs, calcite and (metastable) aragonite. Experiments are proposed to monitor surface reaction morphology and kinetics in the presence of isolated simple acidic and basic amino acids, that are candidates for directing growth in natural systems. In order to characterize dynamic nanoscale growth morphologies and mechanisms, atomic force microscopy (AFM) observations are proposed under in situ conditions. The combination of mechanism and rate determinations are important for understanding and predicting controls by organic molecules on natural precipitation and dissolution of calcite and aragonite, and provide new constraints on models of bonding and reactivity at the nanoscale in organized structures.

Keywords: Biomineralization, Calcium Carbonate, Atomic Force Microscopy, Surface Reactions

178. **REACTIONS AND TRANSPORT OF TOXIC METALS IN ROCK-FORMING SILICATES AT 25°C**
$200,000
DOE Contact: W. C. Luth, (301) 903-5822
Johns Hopkins Contact: D. R. Veblen, (410) 516-8487
Lehigh University Contact: E. Ilton, (610) 758-5834

Heterogeneous electron-cation transfer reactions between aqueous metals and silicates can be responsible for the retention or mobilization of multivalent cations in the near-surface environment. Reaction mechanisms are investigated as a basis for models of aqueous metal-mineral transport processes applicable to a wide range of problems, from toxic metal migration in aquifers to scavenging of heavy metals from industrial solutions. Specific reactions to be investigated are aqueous Cr(III), Cr(VI), Cd(II), Se(VI), Co(II) solutions with specified surfaces of representative phyllosilicates biotite, and chain silicates pyroxene and amphiboles. As an outgrowth of this investigation, a widely applicable analytic tool is to be developed for measuring Fe(II)/Fe(III) concentrations of small areas (approximately 25 X 50 micron) of silicates in thin sections with x-ray photoelectron spectroscopy (XPS).

Keywords: Surface Reactions, High-Resolution Transmission Electron Microscopy, Phyllosilicates, Chain Silicates

179. **THE CRYSTAL CHEMISTRY AND STRUCTURAL ANALYSIS OF URANIUM OXIDE HYDRATES**
$100,000
DOE Contact: W. C. Luth, (301) 903-5822
University of New Mexico Contacts: D. Miller and R. C. Ewing, (505) 277-4163

Systematic crystal chemical relationships among uranium oxide hydroxide phases which are initial corrosion products of uraninite ore and spent nuclear fuel, are investigated to help constrain systematic models for crystal structure topologies. Current work involves the determination of crystal structures for identified key missing phases, such as ianthinite and schoepite, which contain oxidized U^{6+} and are among corrosion products of UO_2 in near-surface, oxidizing environments. Research objectives are to use the new data on structural topologies to interpret and predict speciation and thermodynamic stability relations among uranium oxide hydrates.

Keywords: Uranium Oxide Hydrates, Crystal Chemistry, Structural Topology

MATERIALS PROPERTIES, BEHAVIOR, CHARACTERIZATION OR TESTING

180. **CATION DIFFUSION RATES IN SELECTED SILICATE MINERALS**
$95,000
DOE Contact: W. C. Luth, (301) 903-5822
Sandia National Laboratory Contacts:
Randall T. Cygan, (505) 844-7216 and
H. R. Westrich, (505) 844-9092

Objectives of this research are to determine experimental cation diffusion coefficients for garnet and pyroxene minerals at temperatures less than 1000°C for evaluating disequilibrium behavior in geological, nuclear waste, energy, and materials applications. A new thin-film technique for preparation of diffusion couples was developed in order to measure the relatively slow diffusion of Mg^{2+}, Mn^{2+}, and Ca^{2+} in garnets and pyroxenes. Depth profiles of tracer isotopes are then evaluated using an ion microprobe. Comparison of the diffusion coefficients determined under various oxygen fugacities provides information about the diffusion mechanism and the defect structure of the mineral sample. Results suggest a slower mechanism for magnesium diffusion in pyrope for relatively reducing conditions.

Keywords: Cation Diffusion, Garnets, Pyroxenes, Silicate Minerals, Diffusion Mechanism, Defect Structure

181. **SHEAR STRAIN LOCALIZATION AND FRACTURE EVOLUTION IN ROCKS**
$85,404
DOE Contact: W. C. Luth, (301) 903-5822
Northwestern University Contact: J. W. Rudnicki, (708) 491-3411

Prediction of the causative stresses, location, orientation, thickness, and spacing of fractures in fault zones is important to energy production, waste disposal, and mineral technologies. This study examines the relation of fractures to the macroscopic constitutive description and microscale mechanisms of deformation by testing a standard theory of localization that describes faulting as an instability of the constitutive description of homogeneous deformation. A new, more realistic nonlinear constitutive model, based on the growth and interaction of microcracks which produces increased bulk compliance, is being developed and calibrated with axisymmetric compression tests. Numerical studies (at SNL) will evaluate the complications of realistic geometries and boundary conditions. Preliminary results suggest that the response to an abrupt change in the pattern of deformation is completely nonlinear and cannot be approximated accurately by incrementally linear models, as is often done. This nonlinear response may therefore be critical to the evolution of typical fault zones.

Keywords: Shear Strain Localization, Fracture Evolution, Constitutive Description, Nonlinear Behavior

182. **OXYGEN AND CATION DIFFUSION IN OXIDE MATERIALS**
$171,000
DOE Contact: W. C. Luth, (301) 903-5822
LLNL Contact: F. J. Ryerson, (510) 422-6170
University of California at Los Angeles Contact: K. D. McKeegan, (310) 825-3580

The objective of this work is to measure the diffusion parameters for various cations and oxygen in important rock-forming minerals to constrain both geochemical transport processes and diffusive mechanisms affecting physical properties such as creep and electrical conductivity. Oxygen self-diffusion coefficients have been measured for three natural clinopyroxenes, a natural anorthite, a synthetic magnesium aluminate spinel, and a synthetic akermanite over oxygen fugacities ranging from the Ni-NiO to Fe-FeO buffers. The oxygen self-diffusion coefficients of the three clinopyroxenes are indistinguishable. At a given temperature, oxygen diffuses about 100 times more slowly in diopside than indicated by previous bulk-exchange experiments. New data for anorthite, spinel, and akermanite agree well with prior results obtained by gas-solid exchange and depth profiling methods at different oxygen fugacities, indicating that diffusion of oxygen in these nominally iron-free minerals is not greatly affected by fO_2

Keywords: Diffusion, Minerals, Plastic Deformation

183. **DISSOLUTION RATES AND SURFACE CHEMISTRY OF FELDSPAR GLASS AND CRYSTAL**
$114,700
DOE Contact: W. C. Luth, (301) 903-5822
Penn State Contact: S. Brantley, (814) 863-1739

Dissolution rates and mechanisms of the most common crustal mineral group, the feldspars, (Na,K,Ca) (Al,Si)$AlSi_2O_8$, are key factors in environmental simulations of coupled fluid flow, effective water-rock surficial area, and fluid residence times. New dissolution experiments and characterization of these silicate mineral and glass surfaces and solutions are underway in order to help resolve discrepancies between existing laboratory measurements that are much faster than dissolution rates observed in the field for feldspars in soils, aquifers and small watersheds. Characterization of the laboratory-reacted solids and naturally weathered feldspars by IR and neutron methods for water content, and XPS and mass spectrometric methods for composition-depth profiling of leaching and surface adsorption complemented with surface analysis by field-emission SEM and AFM methods, will be used to constrain rate-controlling mechanisms of dissolution. Mechanistic information provided with a variety of micro-analytic methods that can encompass mechanisms of dissolution from glass to crystal and from laboratory to field environments will help to determine which of several competing dissolution models best describes the natural weathering process.

Keywords: Silicate Minerals, Dissolution Rates, Dissolution Mechanism, Surface Reactions, Surface Characterization

184. **THERMODYNAMICS OF MINERALS STABLE NEAR THE EARTH'S SURFACE**
$150,000
DOE Contact: W. C. Luth, (301) 903-5822
Princeton University: A. Navrotsky, (609) 258-4674

The purpose of this work is to expand our data base and understanding of the thermochemistry of minerals and related materials through a program of high temperature solution calorimetric studies. The technique of oxide melt calorimetry (in molten $2PbO \cdot B_2O_3$) has been extended to volatile-bearing phases. Measured mixing enthalpies of amphibole solid solutions are insensitive to OH-F substitution, but depend strongly on alkali ion substitution in the large A-site. Measured mixing enthalpies of open-framework zeolites are insensitive to species incorporation in the cavities, suggesting that there are few limitations on the variety of (metastable) structures that can be synthesized. Measured mixing enthalpies of damaged zircons are on the order of twice the heat of formation from component oxides, consistent with damage on the scale of near-neighbors and with greatly increased solubility in aqueous fluids.

Keywords: Thermochemistry, Solution Calorimetry, Amphiboles, Micas, Zircons

185. **THREE-DIMENSIONAL IMAGING OF DRILL CORE SAMPLES USING SYNCHROTRON-COMPUTED MICROTOMOGRAPHY**
$177,200
DOE Contact: W. C. Luth, (301) 903-5822
BNL Contact: Keith Jones, (516) 282-4588
SUNY, Stony Brook Contact: W. B. Lindquist, (516) 632-8361

Synchrotron radiation makes feasible the use of high resolution computed microtomography (CMT) for non-destructive measurements of the structure of different types of drill core samples. The goal of this work is to produce three-dimensional images of rock drill core samples with spatial resolution of 1 micron. CMT images are postprocessed (filtered) to provide specific grain/pore identification to each voxel in the image The pore topology is analyzed statistically to yield information on disconnected pore volumes, throat areas, pore connectivity and tortuosity. Current effort is on development of software to analyze the 3-dimensional connectivity and shape of the pore space using the medial axis theorem from computational geometry.

Keywords: Synchrotron Radiation, Computed Microtomography, Pore Structure, Drill Cores

186. **TRANSPORT PHENOMENA IN FLUID-BEARING ROCKS**
$139,680
DOE Contact: W. C. Luth, (301) 903-5822
Renssalaer Polytechnic Institute Contact:
E. B. Watson (518) 276-6475

The research involves two parts: (1) determining the solubility and diffusivity of selected rock-forming minerals and mineral assemblages in deep C-O-H fluids, and (2) measuring the permeability of fluid-bearing synthetic rocks. A new procedure is being developed for measuring mineral solubilities and component diffusivities in fluids at pressures above 1 GPa, by measuring the total mass of transported component across a thermal gradient in dumbbell-shaped capsules at constant P (>1 GPa). Diffusivities are obtained from independent measurements of the component flux through different T gradients. In the second portion of the investigation, rocks synthesized at high (P > 1 GPa) pressures in the presence of differing fluid compositions and consequently porosity structure, will be analyzed at ambient conditions to determine permeability using dihedral angle measurements and bulk fluid (air) diffusion through the samples. Direct imaging of the pore structure will also be attempted with Scanning Electron Microscopy and synchrotron x-ray tomography.

Keywords: Diffusivity, Solubility, C-O-H Fluids, Porosity Structure, Rock Permeability

187. **STRUCTURE AND REACTIVITY OF FERRIC OXIDE AND OXYHYDROXIDE SURFACES: QUANTUM CHEMISTRY AND MOLECULAR DYNAMICS**
$142,500
DOE Contact: W. C. Luth, (301) 903-5822
PNNL Contacts: Jim Rustad and Andrew Felmy,
(509) 376-1134

The research is a theoretical investigation of the surface structure and reactivity of proton binding sites of ferric oxides and hydroxides. The surfaces of these common minerals are known to bind metals, oxy-anions, and organic chelates through mechanisms that are as yet poorly understood. The approach combines crystalline Hartree-Fock calculations for the ferric (hydr)oxides with a molecular dynamics (MD) model for water currently being developed in collaboration with J. W. Halley of the University of Minnesota, in order to evaluate: (1) structures and relative stabilities of various ferric (hydr)oxide surfaces; (2) the most reactive sites for proton adsorption, indicated by relative proton affinities in vacuo; (3) solvation corrections to relative surface energies and relative proton binding energies; (4) improvements in thermodynamic models of proton adsorption resulting from better predictions of surface structure, site types, and proton binding energies.

Keywords: Proton Adsorption, Surface Structure, Surface Reactivity, Ferric Oxides, Ferric Hyrdoxides

188. **MICROMECHANICS OF FAILURE IN BRITTLE GEOMATERIALS**
$184,239
DOE Contact: W. C. Luth, (301) 903-5822
SUNY, Stony Brook Contact: Teng-Fong Wong,
(516) 632-8240
SNL Contact: Joanne Fredrich, (505) 846-0965

Differences in the onset of brittle failure in low-porosity and high-porosity rocks depend on the cementation, initial damage state and deformation history. However, efforts to predict failure are hindered by the inability to account for initial crack density and ductile intergranular phases. For example, although cementation increases brittle strength and reduces porosity, the toughening mechanism is not well understood. This project aims to resolve this question with a systematic study of microstructures induced in experimentally deformed samples (both pre- and post-failure) of (1) high-porosity carbonate rocks, in which plastic grain deformation and plastic pore collapse are thought to be important; (2) sandstones of higher porosity but varying degree of cementation; (3) low-porosity crystalline rocks (as a test of models on rocks with distinct mechanical properties).

Keywords: Brittle Failure, Plastic Deformation, Experimental Rock Deformation, Cementation

189. **CATION CHEMISORPTION AT OXIDE SURFACES AND OXIDE-WATER INTERFACES: X-RAY SPECTROSCOPIC STUDIES AND MODELING**
$210,000
DOE Contact: W. C. Luth, (301) 903-5822
Stanford University Contacts: G. E. Brown and
G. A. Parks, (415) 723-9168

The research focuses on reactions and reaction mechanisms between aqueous metal ions and oxide surfaces representative of those found in the earth's crust as an aid to developing large-scale models of contaminant transport. Objectives are to (1) characterize reactions by direct sorption measurements, in-situ synchrotron-based x-ray absorption spectroscopy (XAS) of atomic environments at solid-water interfaces, and UV/Vis/IR spectroscopy; (2) investigate how these properties are affected by the solid surface and fluid composition; and (3) develop molecular-scale and macroscopic models for the sorption process. The reactions involve aqueous Co(II) and Pb(II) with Al_2O_3 (corundum), Fe_2O_3, and TiO_2, and the effect of organic liquids. New measurements of Pb(II) sorption on powdered corundum indicate sorption of polymeric species, suggesting that substrate structure is influencing the surface Pb(II) complexation. Comparative studies of the role of organic complexation on the sorption of Cu(II) on the surface of amorphous SiO_2 and on powdered corundum are aimed at specifying surface complexation mechanisms.

Keywords: Surface Complexation, Interface Reactions, Synchrotron X-ray Absorption Spectroscopy

DIVISION OF ADVANCED ENERGY PROJECTS

The Division of Advanced Energy Projects (AEP) provides support to explore the feasibility of novel, energy-related concepts that evolve from advances in basic research. These concepts are typically at an early stage of scientific development and, therefore, are premature for consideration by applied research or technology development programs. The AEP also supports high-risk, exploratory concepts that do not readily fit into a program area but could lead to applications that may span several disciplines or technical areas.

The Division provides a mechanism for exploring the conversion of basic research results into applications that could impact the Nation's energy economy. AEP does not support ongoing, evolutionary research or large scale demonstration projects. Technical topics include physical, chemical, materials, engineering, and biotechnologies. Projects can involve interdisciplinary approaches to solve energy-related problems. The DOE Contact for this program is Walter M. Polansky, (301) 903-5995.

MATERIALS PREPARATION, SYNTHESIS, DEPOSITION, GROWTH OR FORMING

190. **COMBUSTION SYNTHESIS AND ENGINEERING OF NANOPARTICLES FOR ELECTRONIC, STRUCTURAL AND SUPERCONDUCTOR APPLICATIONS**
$196,000
DOE Contact: Walter M. Polansky, (301) 903-5995
Alfred University Contact: Gregory C. Stangle, (607) 871-2798

The investigation will: (1) produce nanoparticles of multicomponent oxide ceramic materials by a combustion synthesis technique that is readily scaled up; (2) apply proven, in-house grain-boundary engineering methods to fine-tune microstructure evolution during densification; (3) use conventional and rapid sintering techniques to densify consolidated nanoparticle compacts; and (4) characterize the material at each stage. Expected results include: (a) the synthesis of nanoparticles of complex composition for use in several applications (such as $YBa_2Cu_3O_{7-x}$, a high-temperature superconductor with uses, e.g., in magnetic flux trapping and high-speed capacitor applications; yttria-stabilized zirconia for, e.g., high surface toughness materials for high-temperature applications; and $BaTiO_3$, a material expected to possess superparaelectric properties when nanocrystalline); (b) the development and reduction to practice of a generic, widely applicable process; and (c) the evaluation of the energy efficiency and commercialization potential of the process. The proposed study will enlist three U.S.-based companies to aid in focusing the research toward the commercialization of successful research results.

Keywords: Nanoparticles, Ceramics, Superconductors, Electronic Materials

191. **CREATION AND DESTRUCTION OF C_{60} AND OTHER FULLERENE SOLIDS**
$302,000
DOE Contact: Dr. Walter M. Polansky, (301) 903-5995
University of Arizona Contact: Donald R. Huffman, (602) 621-4804

This work will focus on the creation and destruction of fullerenes to produce new materials of interest to the Department of Energy. It is now known that, besides the famous C_{60} molecule (buckminsterfullerene), hundreds of other fullerenes, with masses of up to 600 carbon atoms, are also synthesized in the Krätschmer-Huffman process. The physics underlying the creation of the fullerenes is poorly understood and the major portion of this work will be a systematic study of the process. This will involve construction of a new, fully-instrumented smoke-chamber, that will be used in a methodical exploration of fullerene yield versus production conditions. Recent reports of the successful seeding of chemical vapor deposition (CVD)-grown diamond films using thin films of C_{70}, and of the room-temperature conversion of solid C_{60} into diamond powder via non-hydrostatic compression, indicate that some of the first important commercial applications of the fullerenes may involve their destruction as a means of synthesizing high-performance materials. This work will include a systematic study of the destruction and modification of the various fullerenes by chemical reaction, electromagnetic radiation, and electron bombardment.

Keywords: Fullerenes, Diamond Powders, Buckyballs